

## Up-conversion luminescence from poly-crystalline $\text{Yb}^{3+}$ , $\text{Er}^{3+}$ co-doped $\text{NaGd}(\text{MoO}_4)_2$ by simple solid state method

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The up-conversion (UC) luminescence properties of polycrystalline  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  phosphors synthesized by a simple solid-state reaction method were investigated in detail. Under 980 nm excitation,  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  exhibited weak red emissions near 660 and 670 nm, and strong green UC emissions at 530 and 550 nm corresponding to the intra 4f transitions of  $\text{Er}^{3+}$  ( $4\text{F}_{9/2}$ ,  $2\text{H}_{11/2}$ ,  $4\text{S}_{3/2}$ )  $\rightarrow$   $\text{Er}^{3+}$  ( $4\text{I}_{15/2}$ ). The optimum doping concentration of  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  for highest emission intensity was determined by XRD and PL analysis. The  $\text{Er}^{3+}/\text{Yb}^{3+}$  (10.0/10.0 mol%) co-doped  $\text{NaGd}(\text{MoO}_4)_2$  phosphor sample exhibited strongly shiny green emission. A possible UC mechanism for  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  depending on the pump power dependence was discussed in detail.

**Key words:** Upconversion,  $\text{NaGd}(\text{MoO}_4)_2$ , Two-photon process, Rare earth ion.

### Introduction

The rare-earth doped up-conversion (UC) luminescence has been received much attraction because of their potential in applications such as three dimensional displays [1], laser and optical amplifiers [2], solar cells [3, 4], and bio-technologies [5, 6]. Among them,  $\text{Er}^{3+}$ -doped UC phosphors are very popular due to their abundant energy level for UC luminescence and high luminescent quenching concentration compared to other RE ions [7]. Moreover,  $\text{Er}^{3+}$  ions have a large spectral overlap with  $\text{Yb}^{3+}$  ions, which can enhance the UC efficiency through the energy transfer upconversion (ETU) process.

Recently,  $\text{NaGd}(\text{MoO}_4)_2$  have been studied extensively due to attractive luminescence properties and interesting structure properties, which make them suitable for a number of fields such as electro-optical device or laser host crystal. Also,  $\text{NaGd}(\text{MoO}_4)_2$  can be doped with different rare earth ions to vary its luminescence properties. Therefore,  $\text{NaGd}(\text{MoO}_4)_2$  can be stable matrix for UC luminescence.

In this work,  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  were synthesized by a simple solid-state reaction method. Effects of  $\text{Er}^{3+}/\text{Yb}^{3+}$  concentration on crystal structure and UC emission properties were investigated in detail, and related possible UC mechanism was presented.

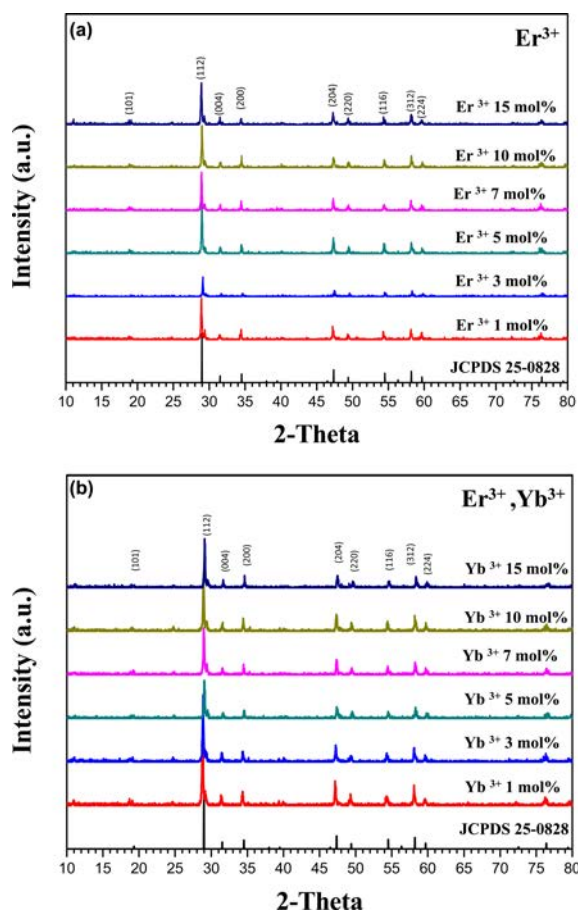
### Experimental procedure

Polycrystalline  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  were synthesized by a simple solid-state reaction method. For the investigation of the UC luminescence with various  $\text{Er}^{3+}/\text{Yb}^{3+}$  concentrations, the molar ratios of the cations were varied as  $\text{NaGd}_{1-x-y}(\text{Er}_x)(\text{Yb}_y)\text{MoO}_4$ . The starting chemicals of  $\text{Na}_2\text{CO}_3$  (Kojundo Chemicals, 99.99%),  $\text{MoO}_3$  (Kojundo Chemicals, 99.99%),  $\text{Gd}_2\text{O}_3$  (Kojundo Chemicals, 99.99%),  $\text{Yb}_2\text{O}_3$  (Kojundo Chemicals, 99.99%) and  $\text{Er}_2\text{O}_3$  (Kojundo Chemicals, 99.99%) were accurately weighted according to their stoichiometric amounts. The raw materials were ground thoroughly by ball-milling and heat-treated at 750 °C for 3 hrs in ambient atmosphere. The phase analysis was conducted using X-ray diffraction (XRD, Rigaku D/MAX2C, Japan,  $\text{Cu-}\alpha$  ( $\lambda = 1.5046 \text{ \AA}$ )). Room-temperature UC luminescent spectra were obtained using a photoluminescence spectrophotometer (PerkinElmer, LS55 with an IR laser diode (980 m, 100 mW)) in a range of 400–700 nm. The pump power dependence was calculated as the irradiation power from 20 to 110 mW (SPEX, 1404p, France)

### Results and Discussion

Fig. 1 shows the phase analysis of  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  with (a) various  $\text{Er}^{3+}$  concentrations up to 15 mol% without  $\text{Yb}^{3+}$  and (b) various  $\text{Yb}^{3+}$  concentrations up to 15 mol% fixed at 10 mol%  $\text{Er}^{3+}$  calcined at 750 °C for 3 h by XRD. It can be seen that their diffraction patterns are in good agreement with the standard diffraction pattern of  $\text{NaGd}(\text{MoO}_4)_2$  (JCPDS: No 25-0828). No impurities or

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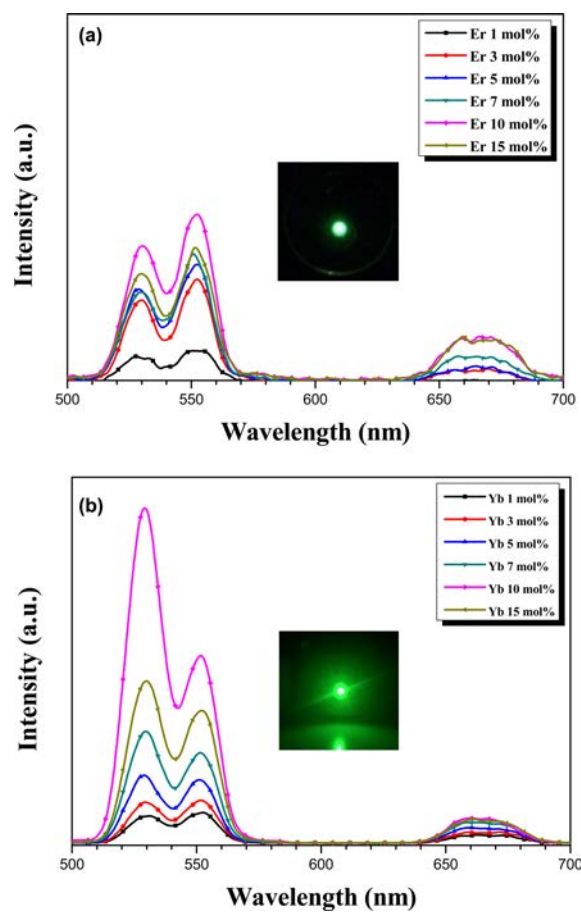


**Fig. 1.** X-ray diffraction patterns of  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  UC phosphors with (a)  $\text{Er}^{3+}$  concentrations from 1.0 to 15.0 mol% and (b)  $\text{Yb}^{3+}$  concentrations from 1.0 to 15.0 mol% fixed at 10.0 mol%  $\text{Er}^{3+}$ .

secondary phases could be identified, which is evidence that single phase  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  with  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  concentrations up to 15 mol% can be obtained.

Fig. 2 shows room temperature UC luminescent spectra of the  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  (a) with  $\text{Er}^{3+}$  concentrations ranging from 1.0 to 15.0 mol% without  $\text{Yb}^{3+}$  and (b)  $\text{Yb}^{3+}$  concentrations ranging from 1.0 to 15.0 mol% fixed with 10.0 mol%  $\text{Er}^{3+}$  under excitation at 980 nm. The UC luminescent spectra of the  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  consisted of three regions [8]: (1) intense green emissions near 530 nm assigned to the  $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$  transition, (2) near 550 nm attributed to the  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$  transition, and (3) relatively weak red emission around 660 and 670 nm attributed to the  $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$  transition, which contribute to the intra 4f-4f transitions of  $\text{Er}^{3+}$  ions. All emission bands are accompanied by several well resolved Stark levels in  $\text{Er}^{3+}$ .

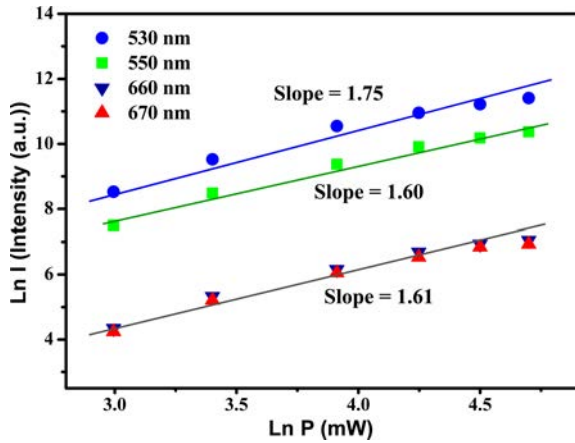
The concentration dependence of up-conversion emissions could be mainly attributed to the interactions between doping ions. As seen in Fig. 2, the UC emission intensity of green emissions near 530 and 550 nm and red emissions around 660 and 670 nm increased with increasing  $\text{Er}^{3+}$  concentration from 1.0



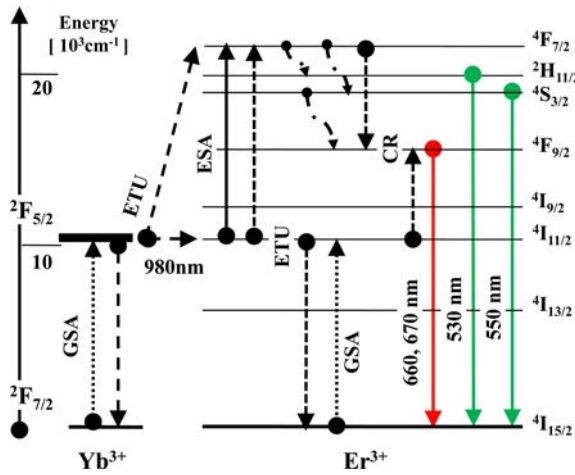
**Fig. 2.** Photoluminescent (PL) spectra of the  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  UC phosphors with (a)  $\text{Er}^{3+}$  concentrations from 1.0 to 15.0 mol% fixed at 10.0 mol%  $\text{Yb}^{3+}$  and (b)  $\text{Yb}^{3+}$  concentrations from 1.0 to 15.0 mol% fixed at 10.0 mol%  $\text{Er}^{3+}$ . The photographs show  $\text{Er}^{3+}$  (10.0 mol%) doped and  $\text{Er}^{3+}/\text{Yb}^{3+}$  (10.0/10.0 mol%) co-doped  $\text{NaGd}(\text{MoO}_4)_2$  UC phosphor samples emit green light excited by a 980 nm laser (100 mW).

to 10.0 mol% and with increasing  $\text{Yb}^{3+}$  concentration from 1.0 to 10.0 mol% then decreased beyond the optimum doping concentration due to the concentration quenching effect [9]. The concentration quenching effect can be explained by the energy transfer between nearest  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  ions. That is, with increasing  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  ion concentrations, the distance between  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  ions will decrease, which can promote non-radiative energy transfer such as exchange interactions or multipole-multipole interactions [10]. Such a result is also observed from  $\text{Er}^{3+}$  doped or  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped in other host matrices [11, 12]. Therefore, according to above mentioned results, the optimum  $\text{Er}^{3+}/\text{Yb}^{3+}$  doping concentration was found to be 10.0/10.0 mol%. The  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  (10.0/10.0 mol%) specimen exhibited a strong green emission shiny to the naked eye when excited by a 980 nm laser diode (100 mW), as shown in inset of Fig. 2(b).

Fig. 3 shows the green and red UC luminescent emission intensities of  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$



**Fig. 3.** Power dependence of the UC emission intensities of the  $\text{Er}^{3+}/\text{Yb}^{3+}$  (10.0/10.0 mol%) co-doped  $\text{NaGd}(\text{MoO}_4)_2$  UC phosphor sample at 530, 550, 660 and 670 nm, respectively.

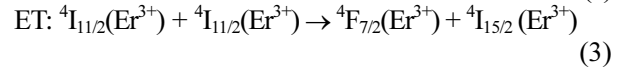
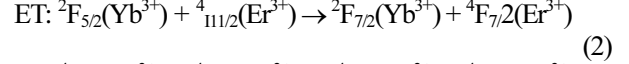
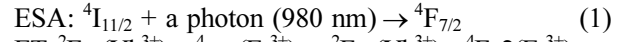


**Fig. 4.** Energy level diagram of  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  in the  $\text{NaGd}(\text{MoO}_4)_2$  crystal and possible UC mechanism under excitation at 980 nm.

(10.0/10.0 mol%) plotted on the logarithmic scale as a function of pump power. In the case of UC process,  $I$  is proportional to the exponent of  $P^n$  [13]. In this equation,  $n$  is the number of pumping photons required to excite the emitting state,  $I$  is the luminescent intensity, and  $P$  is the laser pumping power. The calculated  $n$  values are 1.75 and 1.60, for green emissions at 530 and 550 nm, and 1.61 for emissions at 660 and 670 nm, respectively. The  $n$  values for green emission at 530 nm ( $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$ ), 550 nm ( $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ ) and for red emission at 660 nm and 670 nm ( $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ ) are close to 2, which are in good agreement with previous  $n$  values obtained for green and red emissions in  $\text{Er}^{3+}$  ions [14]. These results indicate that the UC mechanism corresponding to green and red emissions occurs via a two-photon process.

To better comprehend the mechanism which populates the green ( $^2\text{H}_{11/2}$ ,  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ ) and red ( $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ ) luminescence, the UC emission mechanism and population processes for the  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  system are schematically illustrated in Fig. 4. Under excitation at 980 nm,  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  ions are initially

excited from the ground state to the excited state through the ground state absorption (GSA) process ( $\text{Er}^{3+}: ^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ ,  $\text{Yb}^{3+}: ^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ ) or the energy transfer (ET) process of  $^2\text{F}_{5/2}(\text{Yb}^{3+}) + ^4\text{I}_{15/2}(\text{Er}^{3+}) \rightarrow ^2\text{F}_{7/2}(\text{Yb}^{3+}) + ^4\text{I}_{11/2}(\text{Er}^{3+})$  are responsible for the population at the  $^4\text{I}_{11/2}$  level in  $\text{Er}^{3+}$ . For the green emissions, there are three possible processes for the energy transition from the  $^4\text{I}_{11/2}$  level to the  $^4\text{F}_{7/2}$  level of  $\text{Er}^{3+}$ , as follows [15-17].



These three possible processes populate from the  $^4\text{I}_{11/2}$  level to the  $^4\text{F}_{7/2}$  level in the  $\text{Er}^{3+}$  level, and then the  $^4\text{F}_{7/2}$  level relaxes rapidly and non-radiative to the next lower levels at  $^2\text{H}_{11/2}$  and  $^4\text{S}_{3/2}$  in  $\text{Er}^{3+}$  because of short lifetime of the  $^4\text{F}_{7/2}$  level [18]. As a result, the above processes can produce green emissions in the spectral lines near 530 and 550 nm through the radiative transitions of  $^2\text{H}_{11/2}/^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ . For the red emission, the  $^4\text{F}_{9/2}$  level is generated by non-radiative relaxation from the  $^4\text{S}_{3/2}$  to the  $^4\text{F}_{9/2}$  level and cross relaxation (CR) via the  $^4\text{F}_{7/2} + ^4\text{I}_{11/2} \rightarrow ^4\text{F}_{9/2} + ^4\text{F}_{9/2}$  transition in  $\text{Er}^{3+}$  [19]. Finally, the  $^4\text{F}_{9/2}$  level relaxes radiatively to the ground state at the  $^4\text{I}_{15/2}$  level and releases red emission at 660 and 670 nm, as shown in Fig. 2(a,b). The UC emission is dominated to strong green emission at 530 ( $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ ) and 550 nm ( $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ ). The red emissions are very weak due to the weak absorption cross-section of the  $^4\text{I}_{13/2}$  level [20]. Moreover, as the  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  concentration increases up to 10.0/10.0 mol%, the green UC emission dramatically increases compared to the red emission. This is possibly due to the probability of electrons in the  $^4\text{I}_{11/2}$  level being populated to the  $^4\text{F}_{7/2}$  level via the energy transfer UC (ETU) process, which is much higher than that of non-radiative relaxation to the  $^4\text{I}_{13/2}$  level [21].

Moreover, it is worth noting that  $\text{NaGd}(\text{MoO}_4)_2$  can be a great candidate for green UC phosphors and would play important roles in the industrial fields that need green UC phosphors because green emitting property of the  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  does not change with  $\text{Yb}^{3+}$  concentration, while UC emission color of  $\text{Y}_2\text{O}_3$ -like representative oxide UC phosphors change from green to red emission as  $\text{Yb}^{3+}$  doping concentrations [22].

## Summary

$\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  UC phosphors were synthesized by a simple solid-state reaction method. Under NIR excitation (980 nm),  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  phosphors exhibited obviously bright

green UC luminescence at 530 and 550 nm with weak red emission at 660 and 670 nm. It was found that the UC emission intensity depends on  $\text{Yb}^{3+}$  acting as a sensitizer ion to improve the absorption cross-section around 980 nm, while  $\text{Er}^{3+}$  acts as an activator ion for UC luminescent centers in the  $\text{NaGd}(\text{MoO}_4)_2$  matrix. The optimum doping concentrations of  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  for highest green UC luminescence were 10.0 and 10.0 mol%, respectively. The UC emission is dominated by strong green emissions at 530 and 550 nm compared to red emissions at 660 and 670 nm which are resulted from the weak absorption cross-section of the  $^4\text{I}_{13/2}$  level in  $\text{Er}^{3+}$  and the probability that electrons in the  $^4\text{I}_{11/2}$  level get populated to the  $^4\text{F}_{7/2}$  level via the ETU process, which is much higher than that of non-radiative relaxation to the  $^4\text{I}_{13/2}$  level. Moreover, a two-photon process is responsible for both the UC green luminescence generated by  $^2\text{H}_{11/2}$ ,  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$  and the red emission generated by  $^2\text{F}_{7/2} \rightarrow ^4\text{I}_{15/2}$  in  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  phosphors. Therefore, based on our results, it was concluded that  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped  $\text{NaGd}(\text{MoO}_4)_2$  can be an excellent candidate for green UC phosphors.

## References

1. J. Mendez-Ramos, V.K. Tikhomirov, V.D. Rodriguez and D. Furniss, *J. Alloy. Compd.* 440 (2007) 328-335.
2. J.H. Zhang, H.Z. Tao, Y. Chang and X.J. Zhao, *J. Rare. Earth* 25 (2007) 108-120.
3. T. Trupke, M.A. Green and P. Würfel, *J. Appl. Phys.* 92 (2002) 4117-4220.
4. B.S. Richards and A. Shalav, *IEEE Trans. Electron Devices* 54 (2007) 4117-4222.
5. E. Downing, L. Hesselink, J. Ralston and R. Macfarlane, *Science* 273 (1996) 1185.
6. A. Rapaport, J. Milliez, M. Bass, A. Cassanho and H. Jenssen, *J. Disp. Technol.* 2 (2006) 68-70.
7. X. Li, J.Y. Wang and J. Li, *J. Lumin.* 12 (2007) 351-353.
8. H.X. Yang, H. Lin, Y.Y. Zhang, B. Zhai and E.Y.B. Pun, *J. Alloy. Compd.* 453 (2008) 493-498.
9. M. Liu, S.W. Wang, J. Zhang, L.Q. An and L.D. Chen, *Opt. Mater.* 29 (2007) 1352-1355.
10. J.C. Boyer, F. Vetrone, L.A. Cuccia and J.A. Capobianco, *J. Am. Chem. Soc.* 128 (2006) 1352-1355.
11. J.J. Owen, A.K. Cheetham and R.A. McFarlane, *J. Opt. Soc. Am. B* 15 (1998) 684-688.
12. A.S. Oliveria, M.T. de Araujo and A.S. Gouveia, *Appl. Phys. Lett.* 72 (1998) 753-757.
13. S.K. Singh, K. Kumar and S.B. Rai, *Sensors Actuators A: Phys.* 149 (2009) 16-22.
14. M. Rico, J. Liu, J.M. Cano-Torres, A. Garcia-Cortes, C. Cascales, C. Zaldo, U. Griebner and V. Petrov, *Appl. Phys. B* 81 (2005) 621-625.
15. L.H.C. Andrade, M.S. Li, Y. Guyot, A. Brenier and G. Boulon, *J. Phys.: Condens. Matter.* 18 (2006) 7883-7888.
16. Z. Fu, W. Xia, Q. Li, X. Cui and W. Li, *Cryst. Eng. Comm.* 14 (2012) 4618-4622.
17. J. Liu, H. Lian and C. Shi, *Opt. Mater.* 29 (2007) 1591-1595.
18. R.D. Shannon, *Acta Cryst. A* 32 (1976) 751-755.
19. X. -X. Luo and W. -H. Cao, *J. Mater. Res.* 23 (2008) 2078-2088.
20. D. Yang, C. Li, G. Li, M. Shang, X. Kang and J. Lin, *J. Mater. Chem.* 21 (2011) 5923-5928.
21. H. Guo, N. Dong, M. Yin, W. Zhang, L. Lou and S. Xia, *J. Phys. Chem. B* 108 (2004) 19205-19209.
22. Y. Bai, K. Yang, Y. Wang, X. Zhang and Y. Song, *Opt. Comm.* 281 (2008) 2930-2940.
23. F. Auzel, *Chem. Rev.* 104 (2004) 139-149.
24. F. Wang and X. Liu, *Chem. Soc. Rev.* 38 (2009) 976-980.
25. G.Y. Chen, H.C. Liu, H.J. Liang, G. Somesfalean and Z.G. Zhang, *Solid State Comm.* 196 (2008) 148-155.
26. V. Singh, V.K. Rai, K.A. Shamery, J. Nordmann and M. Haase, *J. Lumin.* 131 (2011) 2679-2689.
27. Q. Sun, X. Chen, Z. Liu, F. Wang, Z. Jiang and C. Wang, *J. Alloy. Comp.* 509 (2011) 5336.
28. S. Das, A.A. Reddy and G.V. Prakash, *Chem. Phys. Lett.* 504 (2011) 206.
29. H. Song, B. Sun, T. Wang, S. Lu, L. Yang, B. Chen, X. Wang and X. Kong, *Solid State Comm.* 132 (2004) 409.